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**SEPARATION OF VANADIUM,  
ZIRCONIUM, TITANIUM, MOLYBDENUM,  
TUNGSTEN, AND COLUMBIUM BY  
ELUTION DEVELOPMENT ION  
EXCHANGE CHROMATOGRAPHY**

**TECHNICAL REPORT**

by

**THOMAS A. FERRARO**

**APRIL 1967**

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ABSTRACT

The elution behavior of vanadium, zirconium, titanium, molybdenum, tungsten, and columbium was studied at various hydrofluoric acid concentrations employing a strong base anion exchange resin. The results of this study were used to establish appropriate separation schemes. Coupled columns were employed for the separation of the complete group. Simple columns were used for less complicated mixtures. Vanadium, zirconium, titanium, and molybdenum were eluted with appropriate hydrofluoric acid solutions. In this way, interference from large amounts of columbium was avoided.

An "interval" equation defining the desired volume interval between successively eluting solutes is offered for calculating the column length required for a particular separation. This equation is especially useful for determining the extent to which a column must be lengthened when overlapping occurs due to high column loading.

## INTRODUCTION

The resolution of mixtures containing vanadium, zirconium, titanium, molybdenum, tungsten, and columbium has always been of interest to the analytical chemist. The analysis of such mixtures has long been one of the most difficult problems in metallurgical analysis. Chemical methods of separation employing precipitating agents are tedious and inefficient.

In recent years refractory-base alloys for high-temperature applications have become increasingly prominent. Columbium-base alloys containing the above elements in various combinations are typical of such materials. This situation emphasizes the need for a method of separation of general applicability to such mixtures.

Ion-exchange chromatography has been the most successful separation technique for this group of elements. Hague and co-workers,<sup>1,2</sup> Wilkins,<sup>3</sup> and Dixon and Headridge<sup>4</sup> have studied the separation of certain of the above elements by means of anion exchange with eluents containing hydrochloric and hydrofluoric acids. Bandi and co-workers<sup>5</sup> proposed an anion exchange separation scheme which employs solutions containing hydrochloric acid and complexing agents as eluents.

However, these methods do not provide for the separation of vanadium, and they are not applicable to mixtures containing large amounts of columbium.<sup>6</sup> This latter statement requires further comment. The hydrochloric-hydrofluoric acid system requires that all of the elements mentioned above be eluted before columbium.<sup>1,3</sup> The elution sequence and eluent compositions are such that intermediate acid mixtures in which columbium adsorption is relatively low cannot be avoided. In the presence of large amounts of columbium this situation leads to early elution of columbium and resultant contamination of other fractions with this element.

To minimize this effect, Dixon and Headridge<sup>4</sup> selected a scheme wherein columbium passes through two such adsorption minima but a third is avoided by eluting molybdenum last. Also, the flow rate is cut down during sample addition and immediately following eluent changes to reduce displacement of columbium. These authors use a column which is 0.5 cm in diameter and 13 cm in length. The method can handle mixtures totaling only a few milligrams, and if columbium is the major constituent, a still smaller amount must be taken to avoid early elution of columbium.

Other disadvantages of this method are that the small column diameter makes it difficult to achieve uniform bed packing, and that channeling at the column wall becomes more serious when the column cross-section is small.<sup>7</sup>

The method of Bandi and co-workers<sup>5</sup> is an interesting application of different complexing agents to the separation of zirconium, titanium, columbium, tungsten, molybdenum, and also tantalum by ion-exchange chromatography. The authors provide data showing satisfactory separation of 20 mg amounts of these elements. They state that mixtures of 200 mg of each of these elements were separated when the concentration of hydrogen peroxide, one of the complexing agents used, was increased. However, optimum peroxide concentrations were not established.

As stated earlier, this method, like the others, does not provide for the separation of vanadium. In addition, the preparation of samples for the ion-exchange separations involves multiple precipitations, ignition, fusion, and leaching.

Accordingly, consideration was given to the possibility of devising a separation scheme which would offer the following advantages over existing methods: provision for the separation of vanadium; ability to deal with large amounts of columbium by means of an elution sequence which avoids passing through adsorption minima of this element; and convenient preparation of the mixture for the ion-exchange separations.

The ion-exchange adsorption characteristics of many elements from various media have been determined and published in the technical literature. On the basis of this information one can often select a system, or combination of systems, which appears most suitable for the resolution of a given mixture of elements. An examination of the adsorption data reported by Faris<sup>8</sup> for the anion exchange-hydrofluoric acid system indicated that this system could be combined with the hydrochloric-hydrofluoric acid system to provide a separation scheme meeting the above requirements.

According to Faris, columbium is strongly adsorbed at all concentrations from 5 to 24 M HF; i.e., its distribution coefficient oscillates between about 300 and 150. On the other hand, the values for tungsten, molybdenum, titanium, and zirconium over the same acid concentrations drop from about 200 down to 20 or less. Vanadium did not yield reproducible values; however, the distribution coefficient values for vanadium IV and vanadium V vary from about 15 for both species to about 2 for vanadium V at 24 M HF and to about 1 for vanadium IV at 15 M HF.

A distribution coefficient of about 5 or less is desirable to facilitate elution of an element from a column. Vanadium meets this requirement at 15 M HF, whereas zirconium and titanium decrease to about 5 to 10 at 24 M HF. The distribution coefficient curves for Mo and W begin to diverge above 15 M HF. Tungsten appears to level off at a value of about 20 in 24 M acid, while Mo decreases to 10 without appearing to level off. If this trend persists above 24 M HF, the maximum employed by Faris, Mo could be eluted at some acid concentration above 24 M, while W would be retained on the column.

It appeared, then, that the anion exchange-hydrofluoric acid system could be employed to separate a mixture of these elements into three fractions, the first containing vanadium, the second zirconium and/or titanium, and the third molybdenum, while tungsten and columbium would be retained on the column. Thus far such a scheme would satisfy the aforementioned requirements; i.e., provision would be made for the separation of vanadium, large amounts of columbium could be handled since this element is strongly adsorbed at all acid concentrations, and hydrofluoric acid would be a convenient solvent for these elements.

The elution of zirconium and titanium in the same fraction is to be expected since their adsorption characteristics are quite similar. This is also the case with the other methods previously mentioned.

The separation of the tungsten and columbium remaining on the column could then be achieved according to existing methods.<sup>1,3</sup> Tungsten would be removed with a mixture of

hydrochloric and hydrofluoric acids containing a sufficient amount of the latter to insure strong retention of columbium.<sup>9</sup> The eluent change from hydrofluoric acid to this acid mixture could not result in an intermediate eluent composition in which columbium adsorption is low, since the concentration of hydrofluoric acid would be sufficiently high in both instances. This is evident upon examination of the anion-exchange adsorption characteristics of columbium in hydrochloric-hydrofluoric acid mixtures as reported by Faris and Brody.<sup>9</sup> The subsequent removal of columbium from the column could be conveniently accomplished by elution with an ammonium chloride-hydrofluoric acid mixture.<sup>1,3</sup>

Since the scheme outlined above appeared feasible and offered the advantages previously mentioned over existing methods, the elution behavior of the elements was studied at various acid concentrations to establish optimum eluent concentrations and column lengths required for the desired separations. Elution schemes were developed for the separation of two or more of the elements vanadium, zirconium and/or titanium, molybdenum, and tungsten from each other and from large amounts of columbium.

### THEORY AND PRELIMINARY CONSIDERATIONS

In elution development chromatography a mixture of ions on a column is separated by passing through the column a solution containing a developing ion which has less affinity for the resin than the ions of the mixture. To give an example of a developing ion, it might be mentioned that the fluoride ion is employed as the developing ion in this work for the separation of vanadium, zirconium, molybdenum, and tungsten with hydrofluoric acid. Normally the mixture to be separated is introduced at the top of the column, and the resin is initially combined with the developing ion. Since the ions of the mixture have a greater affinity for the resin, these species are adsorbed in a band at the top of the column. As development proceeds, the developing ion bypasses the species of the mixture which are more strongly adsorbed. The species of the mixture migrate more slowly; that which is most strongly preferred by the resin is slowest. Eventually the mixture separates into individual bands which travel at different rates, the distance between the bands increasing as they move further down the column.

The bands spread out as they move down the column. In the effluent, the ions of the mixture appear in individual bands, accompanied by the developing ion. Complete resolution of the mixture can be obtained under appropriate conditions. Sharp elution maxima or peaks are obtained when the ion-exchange rates are high and the migration rates are low. The use of a resin of high capacity and small particle size, and low flow rate thus favor clean separations. The distance between bands and thus the separation efficiency increases with increasing column length, although the peaks flatten out more as the distance travelled increases. Operating conditions should be chosen which allow separations with essentially no overlap of neighboring bands and at the same time avoid unnecessary intervals between the bands in order to save time and reagents.

Although a general and rigorous quantitative theory of ion exchange is not yet available, many theories, based on various simplifications or empirical approaches, have been developed. These theories can be used to determine, within limits, the column length required for a particular separation.

Many theories are based on the assumption of linear ion-exchange isotherms, since their application requires that the distribution coefficient of a given solute should be independent of the absolute solute concentration. Generally, this condition is satisfied if the solute occupies about 3 percent or less of the total column resin capacity.<sup>10</sup>

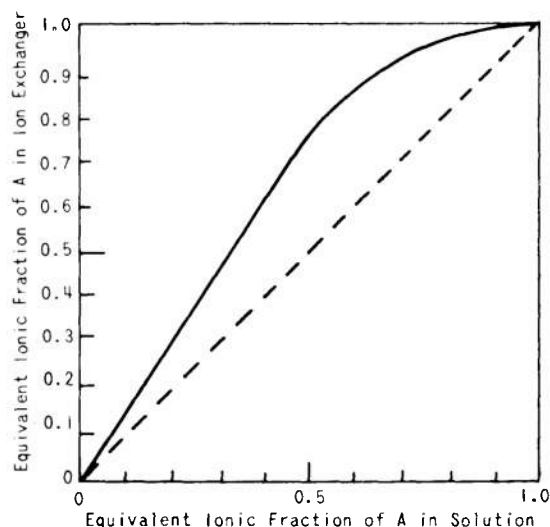


Figure 1. ION-EXCHANGE ISOTHERM

The ion-exchange isotherm is a graphical representation of ion-exchange equilibrium covering the full range of adsorption of a given solute by a resin at a given temperature. Generally, the equivalent ionic fraction of the solute in the ion exchanger is plotted as a function of the equivalent ionic fraction of the solute in the solution, other variables being kept constant. Figure 1 illustrates a typical ion-exchange isotherm.

If the ion exchanger is originally in the B form, i.e., B is the counter ion initially bound to the exchanger, and the latter shows no preference for A or B, then the equivalent ionic fraction of A is the same in both phases. In this case the isotherm is linear and is the diagonal in Figure 1. Actually, however, ion exchangers select one counter ion in preference to another. If ion A is preferred, the isotherm lies above the diagonal and is negatively curved, as shown by the solid line in Figure 1. Selectivity of the ion exchanger therefore requires that the isotherm actually be nonlinear.

In elution development chromatography, the ions of a mixture to be resolved must be preferred above the developing counter ion which is normally also the ion initially bound to the resin. The ions of the mixture must therefore have negatively curved nonlinear isotherms describing the adsorption of these ions in place of the developing counter ion. Moreover, if separation is to occur, the exchanger must discriminate between the species of the mixture. This requires varying degrees of nonlinearity for the isotherms of the different ions. The exchange isotherm of the ion most strongly preferred would show greatest nonlinearity, rising furthest above the diagonal.

The assumption of linear adsorption isotherms, a prerequisite in most theories of ion-exchange column performance, therefore requires that column loading be kept small. In this way, only a short section of the nonlinear isotherms near the origin is involved, and this is generally linear. Thus, it should be noted that this assumption does not imply a lack of selectivity.

The separation of solutes on a column depends on the effluent volume between the peak elution volumes and the shape and width of the individual elution curves. The peak elution volume is the volume of eluent at which the maximum concentration of the individual species appears in the eluate. Elution curves are obtained by plotting concentration of solute in successive fractions of the eluate as a function of total eluate volume.

According to the plate theory, a column is considered to be composed of a number of theoretical plates of resin in which the concentration of solute is taken to be uniform both in the resin and in the interstitial solution volume. The height equivalent to a theoretical plate can



be defined as that length of column in which the resin at the entrance end is in equilibrium with the solution leaving the exit end.

It has been shown that the peak elution volume,  $U^*$ , of a given solute can be predicted by the following expression:<sup>11</sup>

$$U^* = CV + V, \quad (1)$$

where  $C$  is the distribution ratio of the quantity of the solute in the resin of a given plate to the quantity of the same solute in the interstitial volume of the same plate at equilibrium; and  $V$  is the volume of the interstitial liquid phase of a column in milliliters.

When the distribution ratios or coefficients of the solutes are independent of total solute concentration, i.e., at low concentrations, the elution curves of the solutes can be treated as Gaussian normal distribution curves.<sup>10-14</sup>

Rieman and Sargent combined the Gaussian equation with some of the equations of Mayer and Tompkins to obtain a comparatively simple equation of the elution curve<sup>11</sup> (see Figure 9 for some typical elution curves):

$$M = M^* \exp \left\{ -\frac{p}{2} \left( \frac{C+1}{C} \right) \left( \frac{U^* - U}{U^*} \right)^2 \right\}, \quad (2)$$

where  $M$  is the concentration of the solute being eluted at eluate volume  $U$ ;  $M^*$  is the concentration of the solute at the peak elution volume,  $U^*$ ; and  $p$  is the number of theoretical plates in the column.

Letting  $U_a$  be the values of  $U$  corresponding to a solute concentration of  $M^*/e$ , where  $e$  is the base of natural logarithms, the following expression for the number of plates was obtained:

$$p = \left( \frac{2C}{C+1} \right) \left( \frac{U^*}{U^* - U_a} \right)^2. \quad (3)$$

Thus, by determining  $U^*$  and  $U_a$  from an experimental elution curve and calculating  $C$  by Equation 1, the number of plates in the column can be determined by means of Equation 3.

From Equation 2 and the table of probability integrals, the length of column ( $H$ ) required to provide a separation of two solutes with a cross contamination of 0.05 percent has been calculated:<sup>11</sup>

$$\sqrt{H} = \frac{3.29}{C_2 - C_1} \left( \frac{C_2 + 0.5}{\sqrt{P_2}} + \frac{C_1 + 0.5}{\sqrt{P_1}} \right). \quad (4)$$

The subscripts 1 and 2 indicate the solute to which the value refers, i.e.,  $C_1$  is the distribution ratio of the solute which is first to elute and is therefore smaller than that of the second solute,  $C_2$ .  $P$  is the number of plates per centimeter of column:

$$P = \frac{p}{H}. \quad (5)$$

The value 3.29 is the value of the limit of the probability integral where the latter equals 0.9995. By substitution of other limit values the equation can be modified to provide other degrees of cross contamination. For example, by substituting the value 3.74 in place of 3.29, the column length so determined would separate the solutes under consideration with a purity of 99.99 percent or a cross contamination of 0.01 percent.

An experimental elution curve provides two values for  $U_a$ , one value obtained from the leading edge and the other from the trailing edge of the curve. If the elution follows Equation 2 perfectly, the same value for the number of plates would be obtained from Equation 3 for both values of  $U_a$ . However, most experimental curves are subject to some tailing, where the trailing edge is less steep than the leading edge. In this case the  $p$  value corresponding to the smaller  $U_a$  may differ considerably from and will be larger than that obtained with the larger  $U_a$ .

Since the separation of two solutes is dependent upon the trailing edge of the solute which elutes first and the leading edge of the next solute, corresponding  $U_a$  values must be employed in determining the column length required for the separation. In applying Equation 4, therefore, the  $U_a$  following the elution peak of the first solute should be used to determine  $P_1$ , while the  $U_a$  preceding the elution peak of the second solute should be used for  $P_2$ .

With any given column, flow rate, and temperature, different values of  $p$  will generally be obtained with different solutes. In ion exchange the rate of exchange is most often determined by diffusion within the resin particles. Accordingly, the height of a theoretical plate is roughly inversely proportional to the distribution coefficient of the adsorbing species.<sup>14</sup>

## EXPERIMENTAL

### Preparation of Ion-Exchange Columns

Polystyrene tubing 2.5 cm in diameter was used to prepare the columns used in these experiments. The bottom of the tubing was closed with a No. 5 neoprene stopper with a 1/4-inch hole. A 4-inch length of polyethylene tubing with a 1/4-inch outside diameter (1/8-inch bore) was inserted into the hole, flush with the upper surface of the stopper. A 3-inch length of Tygon R tubing was attached to the polyethylene tube and the flow controlled by a pinch-cock on the Tygon tubing. The bottom of the large tube was covered with a layer of acid-resistant vinyl chloride plastic "wool". The column was filled with 270-mesh Dowex-1 resin of 8 to 10 percent crosslinkage to obtain a settled column of the resin of the desired height. The selection of the 270-mesh particle size was based upon considerations already discussed regarding the advantage of small particle size.

### Measurement of Exchange Capacity and Interstitial Volume

The capacity and interstitial volume were determined for a column containing a resin bed approximately 11 cm high.<sup>11</sup> A dilute hydrochloric acid solution was passed through the resin until the HCl concentration of the effluent equaled that of the influent ( $\sim 0.1$  N). The chloride adsorbed by the resin and the HCl in the interstitial solution were displaced by elution with a  $\text{NaNO}_3$  solution ( $\sim 1$  N).  $\text{AgNO}_3$  was used to test for complete chloride removal. The concentration of the hydrogen and chloride ions in the collected eluate was determined titrimetrically

in appropriate aliquots. The interstitial column volume was determined from the total hydrogen ion concentration. The column capacity was obtained from the total chloride concentration after correcting for the chloride contributed by the free acid.

The interstitial volume was determined to be 46 percent of the bed volume and the capacity 1.5 milliequivalents per milliliter of bed volume or 7.6 milliequivalents per centimeter of column length for a 2.5-cm diameter column.

#### General Experimental Procedure

The subsequent elution and separation studies were performed according to the general procedure described herein.

Solutions containing the desired elements in each case were prepared by dissolving the pure metals in a mixture of hydrofluoric and nitric acids in Teflon beakers. These solutions were then evaporated to dryness and the residue dissolved in dilute hydrofluoric acid.

In each case the sample solution was then transferred to an appropriate preconditioned column and the eluting acid (eluent) was then passed through the column. The solution leaving the column, i.e., the eluate, was collected in 25-ml fractions. Collection of fractions was begun with the addition of the sample. A flow rate of 2.5 ml/minute was maintained in each case. This corresponds to 0.5 ml/sq cm/min, which is a relatively slow flow rate and typical of that used in other ion exchange investigations.<sup>10</sup>

The elution behavior of the elements was determined by testing these fractions for each of the elements involved. The manner of testing depended upon the type of information being sought. Where quantitative data was needed in order to define individual elution curves for the purpose of calculation, the elements were determined by photometric methods. Otherwise, semi-quantitative chemical tests were employed to establish the presence or absence of an element. In this case, estimates of relative amounts were made on the basis of visual comparison for the purpose of preparing elution curves. The chemical tests employed are described in Appendix I and Appendix II.

In the separation studies the amount of columbium taken was generally such as to provide a total mixture of one gram. This sample size was selected as convenient for practical analytical applications.

The use of highly concentrated hydrofluoric acid solutions in the methods proposed herein may be considered by some to present a problem. However, many ion-exchange procedures involve the use of highly concentrated acid solutions. For this reason all ion exchange work in this laboratory is performed in a chemical hood constructed of clear plastic. Sample preparations are performed in an adjacent hood. By taking appropriate precautions these methods can be employed with no difficulty.

## Separation of Vanadium

### A. Initial Group Elution Studies with 15 M and 20 M HF

A tentative separation scheme was devised based on the distribution coefficient data of Faris. The first step of this scheme involves the separation of V from Zr, Ti, Mo, W, and Cb by elution of V with 15 M HF.

The feasibility of this approach was evaluated by application to two sample solutions. Each contained 50 mg each of V, Mo, and W and 800 mg of Cb in 75 ml of 3 M HF. In addition, one sample contained 50 mg of Ti, the other 50 mg of Zr. The samples were transferred to columns containing resin beds 20 cm in height which had been preconditioned by passing 100 ml of 3 M HF through each column in 25-ml increments. Elution with 15 M HF was begun when the addition of the sample to the columns was complete.

Vanadium was present essentially in the quinequivalent state due to the oxidizing conditions employed in the preparation of the samples. It appeared as a dark band on the column and was observed to elute much more slowly than had been expected on the basis of published data.<sup>8</sup> An eluate volume of about 700 ml was collected before complete removal of vanadium from the column was effected.

Qualitative chemical tests showed that zirconium began to elute immediately after the last of the vanadium had been removed, while titanium and vanadium were separated by about 25 ml. Molybdenum, tungsten, and columbium were not detected in any of the fractions, thus indicating that they had been successfully retained on the column.

Although the separation of vanadium from the other elements was achieved, it would be desirable to have a greater latitude, say 50 ml or better, in the separation of vanadium from zirconium and titanium, and also to be able to elute vanadium more rapidly. The former could be achieved by increasing the length of the resin bed but this would entail a corresponding increase in the eluent volume required to remove vanadium. Thus a change in eluent concentration was next considered.

The relative ease of separation of two species can be evaluated by means of the ratio of the distribution coefficients referred to a common ion, often termed the separation factor.

At low acid concentrations, the distribution coefficient curve of vanadium diverges sharply from those of zirconium, titanium, molybdenum, and tungsten.<sup>8</sup> Thus, the separation factor of zirconium and vanadium increases with decreasing eluent concentration. It should therefore be possible to separate these elements with a shorter column and possibly with a smaller eluent volume at an acid concentration below 15 M HF, provided the elution rate of vanadium is not excessively lowered. It will be recalled that the distribution coefficients decrease with increasing acid concentration, as pointed out in the Introduction.

However, a slight divergence is also indicated toward acid concentrations above 15 M due to the difference in the shape of the vanadium curve as compared with the others. Thus, adequate separation of vanadium and zirconium, but more rapid elution of vanadium, may be possible at a higher eluent concentration. This approach was therefore tested first.

To evaluate the effect as in the previous experiment, the same amounts of vanadium, zirconium, molybdenum, tungsten, and columbium were eluted on a 20-cm column with 20 M HF. As the elution progressed it became apparent that the elution rate of vanadium was not much greater than that observed with 15 M HF. On the other hand, the elution rate of zirconium had been increased to a much greater extent, for it was found that maximum elution of these elements occurred almost simultaneously.

#### B. Elution Behavior of Vanadium and Zirconium at Acid Concentrations Below 15 M

Since increasing the eluent concentration caused overlapping of vanadium and zirconium, attention was next focused on the elution behavior of these two elements at hydrofluoric acid concentrations below 15 M. Hydrofluoric acid concentrations of 5.8 M, 8.7 M, and 11.6 M were employed to determine the individual elution curves. The elution behavior of zirconium in 5.8 M HF was determined with a 3.8-cm column. The sample solution contained 50 mg of zirconium in 10 ml of 3 M HF. In every other case an 11.1-cm column was employed and sample solutions contained 100 mg of the element. Column loading was thus less than 3 percent of the total column capacity in each case, assuming monovalent fluoride species as the adsorbing anions. The concentration of vanadium and zirconium in their respective fractions was determined photometrically and corresponding elution curves were prepared from these data. These are shown in Figures 2 through 4.

The  $U^*$  and  $U_a$  values obtained from the elution curves were corrected for the original sample volume of 10 ml and employed to calculate the appropriate  $C$ ,  $p$ , and  $P$  values at each acid concentration by means of Equations 1, 3, and 5. The required column lengths ( $H$ ) were then calculated by means of Equation 4 and the results increased by 10 percent to allow for experimental error.<sup>11</sup> The  $C$ ,  $p$ ,  $P$ , and  $H$  values obtained are shown in Table I.

Table I. CALCULATED VALUES OF  $C$ ,  $p$ ,  $P$ , AND  $H$

HF Concentration	$C_V$	$C_{Zr}$	$p_V$	$p_{Zr}$	$P_V$	$P_{Zr}$	$H$	$H \times 1.1$
5.8 M	17.3	157	15.7	33.3	1.41	8.8	2.6	2.9
8.7 M	12.5	41.3	25.0	179	2.25	16.1	4.8	5.3
11.6 M	7.7	17.5	26.6	144	2.40	13.0	11.8	13.0

#### C. Effect of Column Loading

It has been pointed out that application of the plate theory requires that column loading be kept low, preferably below 3 percent of the total column capacity. Glueckauf<sup>14</sup> has shown that the extent of column loading is dependent upon the number of theoretical plates and should satisfy the relationship;

$$\frac{\gamma_o}{X} < 1/\sqrt{2p}, \quad (6)$$

where  $\gamma_o$  is the column volume occupied by the original load band and  $X$  is the total column volume. According to this, a column with a large number of plates should be loaded to a smaller extent than one with a small number of plates. For a 5000-plate column,  $\gamma_o$  should be less than 1 percent of  $X$ . However, 5 percent loading will not interfere with the separation performance of a

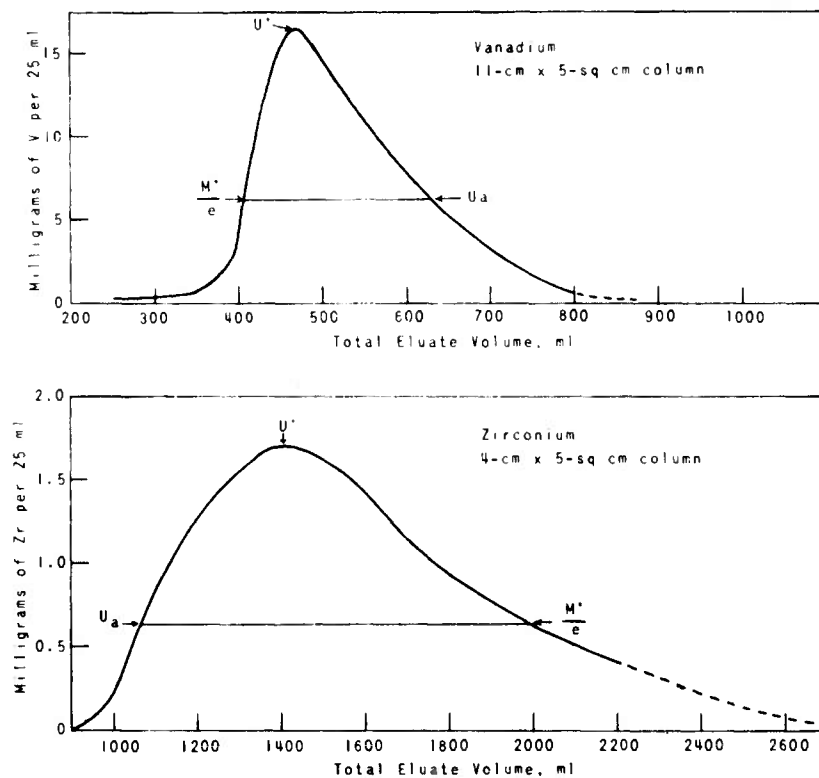


Figure 2. ELUTION OF VANADIUM AND ZIRCONIUM WITH 5.8 M HF

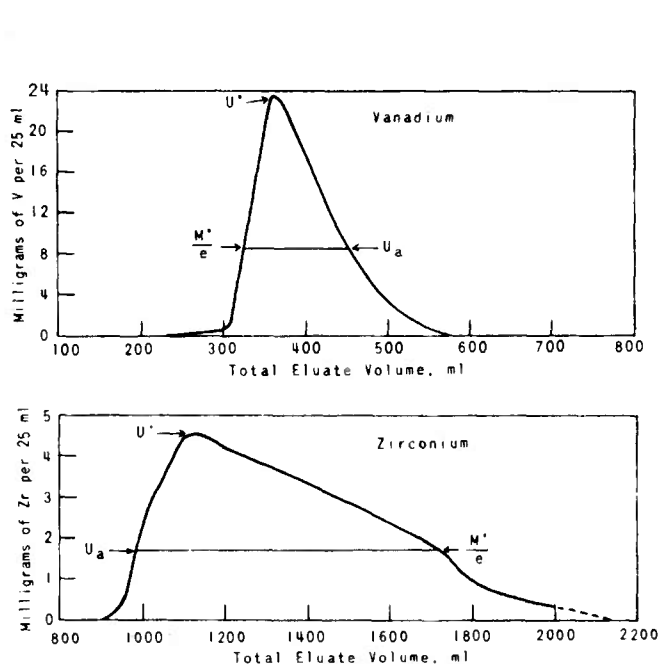


Figure 3. ELUTION OF VANADIUM AND ZIRCONIUM WITH 8.7 M HF ON AN 11-CM X 5-SQ CM COLUMN

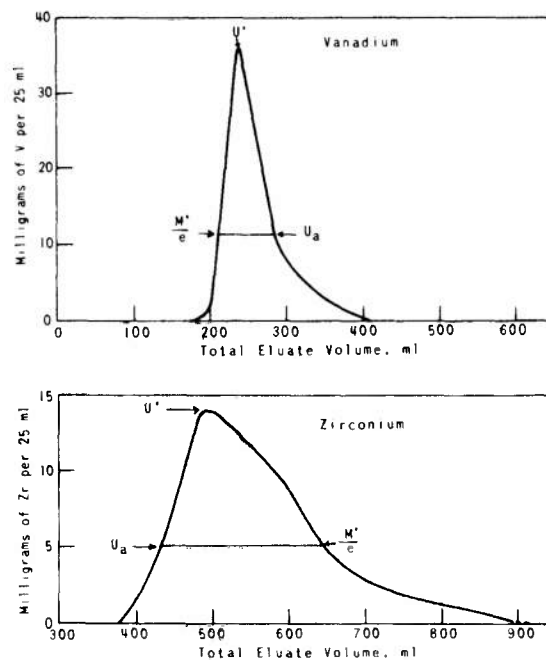


Figure 4. ELUTION OF VANADIUM AND ZIRCONIUM WITH 11.6 M HF ON AN 11-CM X 5-SQ CM COLUMN

200-plate column. Glueckauf points out that even 10 percent loading can be tolerated in the latter case as long as the column can satisfactorily separate trace amounts.

Accordingly, the effect of the desired load level of one gram must be taken into consideration. Assuming a typical mixture to contain 100 mg each of vanadium, zirconium, molybdenum, and tungsten, and 600 mg of columbium, approximately 11 milliequivalents of solutes would be loaded on the column, again assuming monovalent anionic species. Since the column capacity has been shown to be 1.5 milliequivalents per milliliter or 7.6 per centimeter (2.5-cm inside diameter), a column 14.5 cm long would be required for 10 percent loading. According to the elution curves the elution of vanadium would require over 1000 ml of 5.8 M HF or well over 800 ml of 8.7 M HF for a column of this length.

It was decided to evaluate the effect of overloading on the separation of vanadium and zirconium with 8.7 M HF to facilitate the selection of a suitable combination of eluent concentration and column length. It was calculated that a 5.3-cm column would be required for the separation of these elements at appropriate loading levels. At significant load levels, i.e., greater than trace amounts, the column length determined on the basis of the plate theory should be increased by an amount equal to one-half the height of the original load band.<sup>14</sup> Although this still assumes that column loading is 3 percent or less, a corresponding adjustment was made for the much higher load in this case. Thus a load of 11 milliequivalents would occupy  $11/7.6$  or 1.45 cm of column, assuming 100 percent loading efficiency. Consequently, an additional 0.7 cm was added to the calculated value of 5.3 cm and a 6-cm column was employed. Column loading would thus amount to about 24 percent for a typical one-gram sample.

A sample containing 100 mg each of vanadium, zirconium, molybdenum, and tungsten, and 600 mg of Cb in 30 ml of 3 M HF was transferred to a preconditioned 6-cm column. Eluate fractions were collected and analyzed as elution with 8.7 M HF progressed. The resulting data for vanadium and zirconium are plotted in Figure 5. Note that the elution curves overlap considerably. If the eluate were separated into two fractions at a point such as to provide equal purity in each, slightly above 250 ml, the cross contamination would be about 4 to 5 percent, in terms of milliequivalents.

If one were to apply Equations 1, 3, and 4 and the elution curves of Figure 5 to calculate the column length required for the separation of vanadium and zirconium with 8.7 M HF, one would arrive at the surprising figure of 25 cm. This serves to emphasize that the plate theory cannot be applied except under low-load conditions.

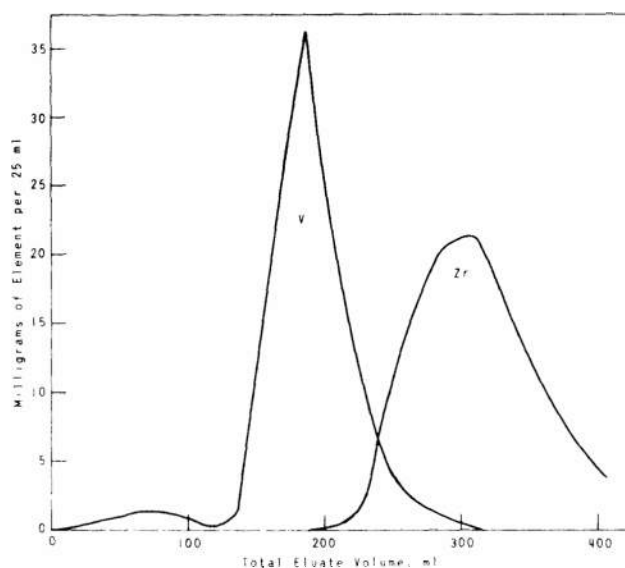


Figure 5. SEPARATION OF VANADIUM AND ZIRCONIUM WITH 8.7 M HF ON A 6-CM X 5-SQ CM COLUMN

The peak elution volumes of Figure 5 and the distribution ratios obtained from Figure 3 were used to determine the "effective" or "apparent" interstitial column volumes for vanadium and zirconium by means of Equation 1. The effective column lengths were then determined by multiplying the actual length by the ratio of the apparent interstitial volume to the actual interstitial volume (13.8 ml). The effective column lengths so determined were 4.8 cm for vanadium and 2.8 cm for zirconium. Since the effective column length was found to be 3.2 cm shorter than the actual column for zirconium, it was reasoned that an effective column length of 6 cm could be achieved simply by increasing the original column length to 9.2 cm.

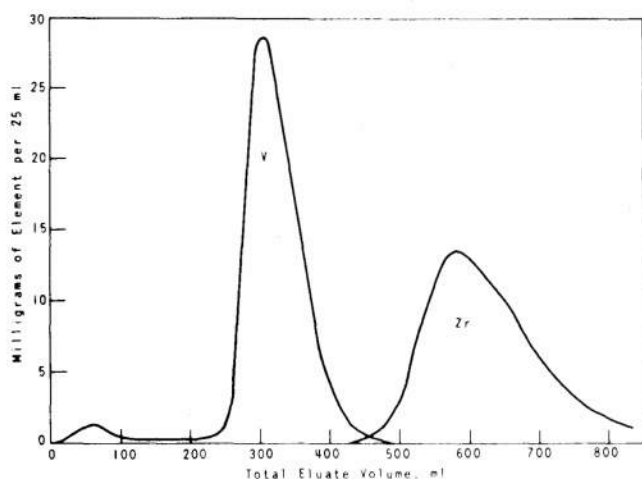


Figure 6. SEPARATION OF VANADIUM AND ZIRCONIUM WITH 8.7 M HF ON A 9-CM X 5-SQ CM COLUMN

Accordingly, another sample was prepared having the same composition as the previous sample. This was transferred to a preconditioned 9-cm column and eluted with 8.7 M HF. Fractions were collected and analyzed photometrically. It was anticipated that some overlap of the elution curves would again occur due to the difference in the effective column length found for each element, as noted earlier. The experimental elution curves shown in Figure 6 do overlap, but the separation is much improved. Here the cross-contamination is about 0.5 percent. The effective column lengths were determined in this case to be equal to the actual column length for vanadium and 5.7 cm for zirconium. Column loading amounted to 16 percent.

On the basis of Figures 5 and 6 it was estimated that the quantitative separation of vanadium with 8.7 M HF would require a column about 12 cm long given a similar mixture of vanadium, zirconium, molybdenum, tungsten, and columbium. However, according to Figure 3, the removal of vanadium would involve the collection of well over 600 ml of eluate, allowing for the sample volume. Column loading in this case would amount to 12 percent.

If 12 percent is taken as the maximum allowable load level, it should be possible to employ an eluent of higher concentration to enhance the removal of vanadium, provided adequate separation could be expected at low load levels. Allowing 0.7 cm for initial column loading, a 13.7-cm column would be required for the separation of vanadium and zirconium with 11.6 M HF. Thus, this eluent could not be expected to provide a quantitative separation with a 12-cm column at 12 percent loading. The most suitable acid concentration must be between 8.7 M and 11.6 M. The median hydrofluoric acid concentration of 10.1 M was therefore applied to the separation of vanadium and zirconium in another sample with composition similar to that used in the previous two experiments. The column length employed was 12.5 cm, allowing 0.5 cm for irregularities observed in the top and bottom edges of the resin bed.



This system yielded the experimental results shown in Figure 7. Note that an eluate volume of about 50 ml separates the elution curves of vanadium and zirconium, and that the elution of vanadium is complete at an eluate volume of 525 ml. This is a considerable improvement over the 700 ml required with 15 M HF, especially in view of the fact that in the latter case only 50-mg amounts of the elements were taken and there was no latitude in the separation of vanadium and zirconium.

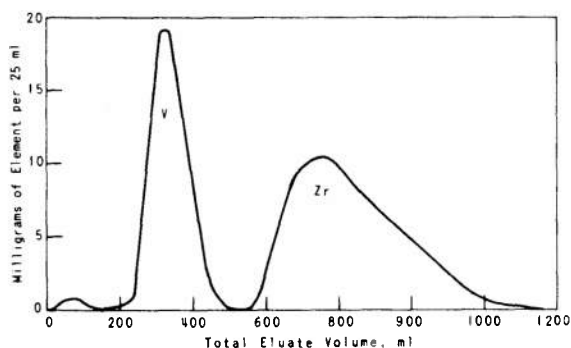


Figure 7. SEPARATION OF VANADIUM AND ZIRCONIUM WITH 10.1 M HF ON A 12.5-CM X 5-SQ CM COLUMN

#### Separation of Ti, Mo, and W

##### A. Initial Group Elution Study with 24 M HF

According to the tentative separation scheme initially devised, the removal of V is followed by elution of Zr and/or Ti with 24 M HF. The Mo would be removed in a third fraction with a stronger HF solution, and the subsequent separation of the W and Cb remaining on the column would be accomplished by established methods.<sup>1,3</sup>

Elution with 24 M HF must not only provide for the separation of Zr and/or Ti from the other elements on the column but it must also allow the subsequent separation of these other elements. Since the distribution coefficients of Mo and W are rather low at this acid concentration,<sup>7</sup> it is to be expected that these elements will be considerably displaced on the column in the course of removing Zr and/or Ti. The Mo should be displaced further than W since its distribution coefficient is lower, but the subsequent separation of these elements would depend on the extent of displacement and the relative proximity of their adsorption bands.

The elution behavior of a mixture of 50 mg each of vanadium, titanium, molybdenum, and tungsten in the presence of 800 mg of columbium with 24 M HF was investigated in order to evaluate the desirability of employing this eluent for the separation of titanium (or zirconium). A 20-cm column was employed. Semi-quantitative chemical tests of the collected fractions were made for the above elements. The relative amount in each fraction was estimated for each element on the basis of visual comparison. The elution curves are shown in Figure 8. To distinguish these curves from those from which quantitative analyses of the fractions were made, the eluate volume is plotted against the estimated percent of each element eluted.

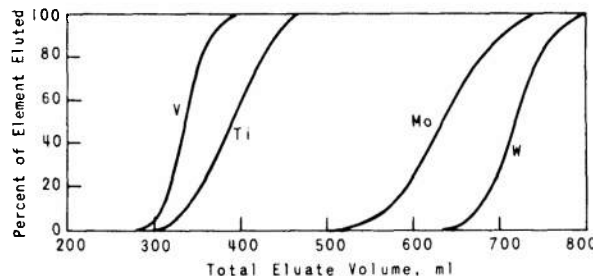


Figure 8. SEPARATION OF TITANIUM AND MOLYBDENUM WITH 24 M HF ON A 20-CM X 5-SQ CM COLUMN

Vanadium was included in this experiment to establish its elution behavior at this acid concentration. This information could prove useful in establishing a separation scheme for mixtures containing no zirconium or titanium.

Figure 8 shows that about 50 percent of the Mo had eluted when W began to appear in the eluate. About 90 percent of the W was removed simultaneously with the remainder of the Mo. Although the desired separation of Ti from Mo was effected, the fact that W follows Mo so closely discourages the use of 24 M HF as the second eluent. In view of the proximity of their adsorption bands, it is not likely that the subsequent separation of these two elements could be achieved except by employing a column of such length as to require the collection of excessively large eluate volumes.

#### B. Elution Behavior of the Elements in 27.5 M HF

It has been pointed out that 24 M HF is the maximum HF concentration employed by Faris in his study of the adsorption of the elements from HF solutions. In view of the results of the previous experiment with 24 M HF, it would be convenient if the separate elution of zirconium and/or titanium could be accomplished with a stronger acid solution. Proper evaluation of this approach required that individual elution curves be determined at an appropriate acid concentration in order to establish the trend of the distribution coefficients above 24 M HF. The acid concentration selected for this study was 27.5 M HF.

With the exception of tungsten, 100 mg of each of the elements vanadium, zirconium, titanium, and molybdenum, dissolved in 10 ml of 3 M HF, were added to separate columns 11 cm long. In the case of tungsten, 200 mg were taken. After transfer of each element to its column, 27.5 M HF was passed through and a series of fractions was collected. The concentration of each element in its respective fractions was determined photometrically. For convenient comparison the individual elution curves are superimposed in Figure 9. In each case column loading amounted to less than 3 percent.

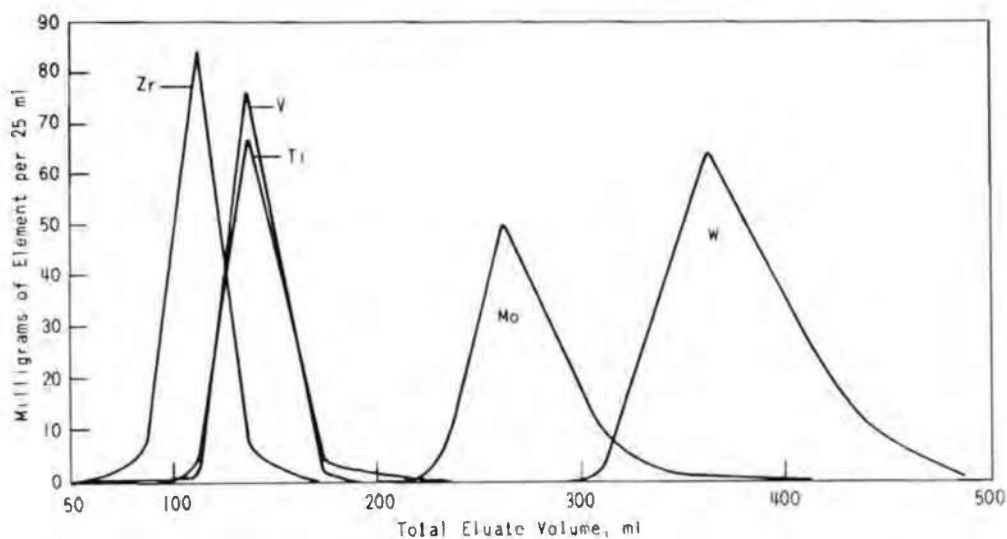


Figure 9. SUPERIMPOSED INDIVIDUAL ELUTION CURVES OBTAINED WITH 27.5 M HF ON AN 11-CM X 5-SQ CM COLUMN

Several conclusions can be drawn from an examination of these elution curves. The divergence of the adsorption behavior of molybdenum and tungsten toward high acid concentrations, as indicated by the distribution coefficient curves reported by Faris, obviously persists above 24 M HF. It is at this higher acid concentration that the separation of these elements becomes feasible.

The separation of zirconium or titanium from molybdenum should also be possible with the same eluent. The resolution of mixtures containing tungsten, together with one of the elements vanadium, zirconium, or titanium, can be accomplished with 27.5 M HF on an 11-cm column, provided column loading is not excessive.

Based on the elution data of Figure 9, the distribution ratios and the number of theoretical plates per centimeter of column length were calculated (Equations 1 and 3). These values are listed in Table II.

Table II. CALCULATED VALUES OF C AND P IN 27.5 M HF

	Zr	V	Ti	Mo	W
C	2.9	3.6	3.9	7.7	12.5
P <sub>1</sub> *	-	12.8	7.7	21.4	20.2
P <sub>2</sub> **	4.4	4.6	3.9	5.8	-

\*The P<sub>1</sub> values are based on the U<sub>a</sub> values obtained from the leading edges of the elution curves.

\*\*The P<sub>2</sub> values pertain to the trailing edges.

The values listed in Table II were used to calculate the column lengths needed to separate Ti and Mo, and Mo and W. These lengths were found to be 13.2 cm for the former and 20.4 cm for the latter. The original calculated values were increased by 10 percent to obtain the above figures. The resolution of a mixture totaling 1 to 2 milliequivalents of Ti, Mo, and W, can be thus accomplished by elution with 27.5 M HF on a 20.4-cm column.

#### C. The Separation of Ti, Mo, and W with 27.5 M HF

The separation of Ti, Mo, and W with 27.5 M HF is shown in Figure 10. A 21.1-cm column was used for the sample containing 100 mg of each of the above elements and 700 mg of Cb in 30 ml of 3 M HF. The calculated column length of 20.4 cm was increased by 0.7 cm, approximately one-half of the length of column occupied by the initial load. Column loading was approximately 7 percent.

Although quantitative separations were achieved, the elution curves are separated by 25 ml or less (see Figure 10). For practical application, when a greater interval between elution curves may be desired, a column length of 24 cm or more would be preferred. As will be demonstrated later, however, smaller amounts of these elements are adequately separated on a 21-cm column. The elution curve of tungsten is shown in Figure 10 to tail somewhat. More efficient removal of this element can be accomplished with an appropriate hydrochloric-hydrofluoric acid solution, such as 7 M HCl-3 M HF,<sup>1</sup> as prescribed in the original scheme.

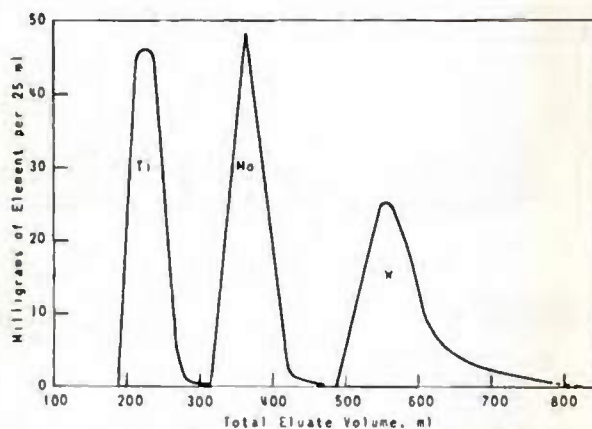


Figure 10. SEPARATION OF TITANIUM, MOLYBDENUM, AND TUNGSTEN WITH 27.5 M HF ON A 21-CM X 5-SQ CM COLUMN



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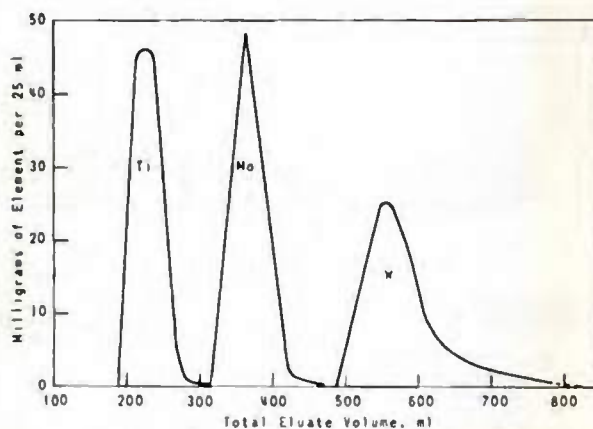


Figure 10. SEPARATION OF TITANIUM, MOLYBDENUM, AND TUNGSTEN WITH 27.5 M HF ON A 21-CM X 5-SQ CM COLUMN

If we let  $U$  equal  $U_V^*$ , the volume of 10.1 M HF required to move the peak of the vanadium band to the bottom of the column, and we substitute  $2.3 H$  for  $V$  in Equation 1 to obtain  $U_V^*$  in terms of  $H$  and  $C_V$ , then the displacement of Mo, up to the point where maximum elution of vanadium occurs, becomes

$$d = \frac{C_V H + H}{C_{Mo}} \quad (9)$$

However, the complete removal of vanadium requires an additional volume of 10.1 M HF beyond this point of peak elution. The additional displacement of Mo resulting from this can also be determined by means of Equation 7 if the volume of eluent is known. The volume of eluent required beyond the peak elution volume to bring the removal of V to 99.95 percent completion can be calculated by

$$U = 3.29 U^* \sqrt{\frac{C}{P H (C + 1)}} \quad (10)$$

where the value 3.29 has the same significance as in Equation 4. Combination of Equation 1 and 10 and substitution of  $2.3 H$  for  $V$  yields

$$U = 7.6 \sqrt{H \frac{(C^2 + C)}{P}} \quad (11)$$

Combining this with Equation 8 and introducing the appropriate distribution coefficients gives

$$d = \frac{3.3}{C_{Mo}} \sqrt{H \frac{(C_V^2 + C_V)}{P_V}} \quad (12)$$

Thus the total displacement of Mo is the sum of Equations 9 and 12. The values for  $C_V$  and  $P_V$  were taken as the average of those determined for 8.7 M and 11.6 M HF. The value of  $C_{Mo}$  was determined in the previous experiment to be 37.

The appropriate values were substituted into Equations 9 and 12 and the displacement of Mo was calculated to be equal to  $0.3 H + 0.6 \sqrt{H}$ . It has been shown that a column length of at least 21.1 cm is required for the separation of Ti, Mo, and W with 27.5 M HF (see Figure 10). Therefore, for the separation of V, Ti, Mo, and W, the column length should be such that at least 21.1 cm of column will be available beyond the location of the Mo band on the column following the elution of V with 10.1 M HF. Thus the column length required would be such that  $0.3 H + 0.6 \sqrt{H} + 21.1 = H$ , or 35 cm.

By means of Equations 1 and 11 it was determined that the elution of V from such a column would require 1200 ml of eluent. At a flow rate of 2.5 ml/min the removal of V along would require 8 hours.

### C. Application of Coupled Columns to the Separation of V, Ti, Mo, and W in the Presence of Cb

Since the use of a 35-cm column involves the collection of a large eluate volume and the expenditure of a great deal of time and reagent, the possibility of employing coupled columns to provide more efficient separations was considered.

There have been several instances in the technical literature involving the use of sectional, or coupled, columns. With the same resin in each section this technique has been employed in displacement development procedures to provide sharper elution bands than are obtainable with single columns.<sup>15</sup> With a cation-exchange resin in one section and an anion-exchange resin in the other, the separation of nonadsorbable, cationic, and anionic species from each other has been achieved in a single pass.<sup>16</sup> Another application employed the same type resin combined with a different counter ion in each section.<sup>17</sup>

For the work described herein, still another manner of employing coupled columns was devised. It was reasoned that a short column could be employed for the separation of V with 10.1 M HF, after which another column could be attached in series with the first column to provide for the subsequent separation of Ti and Mo with 27.5 M HF. Following the removal of Mo, it could be expected, on the basis of previous elution studies, that W would be located in the lower section while Cb would remain in the top section. At this point, then, the sections could be separated and the latter elements eluted simultaneously from each section with appropriate eluents. With this approach, considerable reduction in eluate volume and operating time would be realized. The time required for the separation of V alone would be cut by over four hours by using this technique rather than a single 35-cm column.

The column length required for the separation of vanadium with 10.1 M HF has already been established at 12.5 cm (see Figure 7). For the subsequent separation of titanium or zirconium, molybdenum, and tungsten, at least 21.1 cm, preferably 24 cm, of resin bed should be available in the second section beyond the location of the molybdenum band, following the removal of vanadium with 10.1 M HF.

It has been shown that the displacement of Mo is equal to  $0.3 H + 0.6 \sqrt{H}$ . In this case the length of the first section, H, is 12.5 cm. Thus the displacement of Mo would amount to 5.9 cm. Adding 0.7 cm to allow for one-half the height of the original load band (assuming 100 percent loading efficiency and an 11-milliequivalent load), the estimated position of the Mo band becomes 6.6 cm from the top of the first section. Thus approximately 6 cm of the first section would be available for the subsequent separations. Since 24 cm are desired, the second section should be 18 cm long.

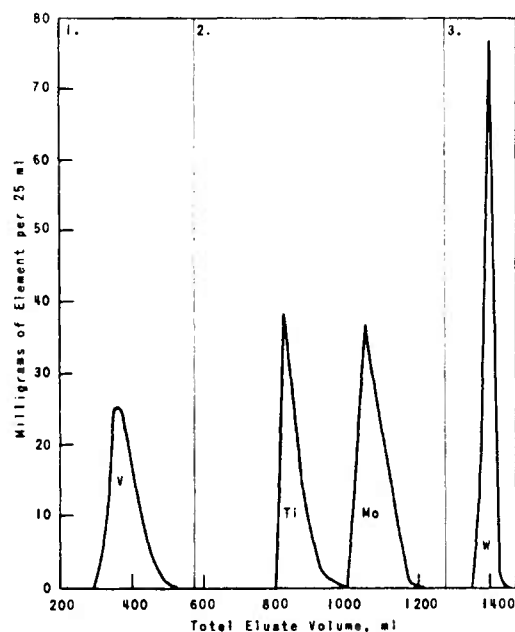
The technique described above was tested on a sample containing 100 mg each of V, Ti, Mo, and W and 600 mg of Cb in 30 ml of 3 M HF. The sample was transferred to a 12.5-cm column which had been pretreated with 3 M HF. The V was eluted with 10.1 M HF, its removal being complete at an eluate volume of about 525 ml.

An 18-cm column pretreated with 27.5 M HF was attached to the bottom of the first column by means of polyethylene tubing fitted in a neoprene stopper which was inserted into the top of the second section. With the sections now connected in series, elution with 27.5 M HF was begun and continued until the Ti and Mo had been eluted. The sections were then separated and W was eluted from the lower section with 7 M HCl-3 M HF. The Cb was eluted from the upper section with 3 M  $\text{NH}_4\text{Cl}$ -1 M HF. The results of tests on the fractions collected at this point showed that all of the Cb had been retained in the upper section while all of the W had passed into the lower section. Photometric analyses of all of the fractions, except those containing Cb from the upper section, produced the elution curves shown in Figure 12. The elution of Cb was followed by testing its fractions with ammonia.

Examination of Figure 12 shows that quantitative separations were achieved, although there is no latitude in the separation of Ti and Mo. Here again improved separation could be realized by increasing the length of the column, i.e., the second section. However, smaller amounts of these elements are adequately separated using an 18-cm column for the second section as was used in this case. This will be demonstrated later. Had 100 mg of Zr been present instead of Ti, there would have been greater latitude in the separation of Zr and Mo, as indicated by Figure 9.

#### Separation Schemes for Various Combinations of Cb and Two or More of the Elements V, Zr and/or Ti, Mo, and W

On the basis of the elution and separation studies conducted, separation schemes were devised for various combinations of Cb and two or more of the other elements studied. All but one of the possible mixtures can be resolved by employing the appropriate scheme selected from those shown in Table III. The presence and subsequent elution of relatively large amounts of Cb with 3 M  $\text{NH}_4\text{Cl}$ -1 M HF is assumed in each case.



**Figure 12. SEPARATION OF VANADIUM, TITANIUM, MOLYBDENUM, AND TUNGSTEN**

1. Elution of V with 10.1 M HF through a 12.5-cm column.
2. Elution of Ti and Mo with 27.5 M HF through coupled 12.5-cm and 18-cm columns.
3. Elution of W with 7 M HCl-3 M HF through lower 18-cm column.

**Table III. SEPARATION SCHEMES**

Column Length (cm)	Eluents	Elements Eluted
<b>Scheme A</b>		
11	1. 27.5 M HF	V, Zr or Ti
	2. 7 M HCl-3 M HF	W
<b>Scheme B</b>		
12.5	1. 10.1 M HF	V
	2. 7 M HCl-3 M HF	Zr or Ti
<b>Scheme C</b>		
21	1. 27.5 M HF	V, Zr or Ti in first fraction Mo in second fraction
	2. 7 M HCl-3 M HF	W
<b>Scheme D</b>		
12.5 cm section	1. 10.1 M HF	V
12.5 cm + 18 cm sections	2. 27.5 M HF	Zr or Ti in first fraction Mo in second fraction
18 cm section	3. 7 M HCl-3 M HF	W

The separation of Ti, Mo, and W by Scheme C is shown in Figure 10, and the application of coupled columns, Scheme D, to the separation of V, Ti, Mo, and W is illustrated in Figure 12. It was mentioned earlier that, although their elution curves do not overlap, a greater interval between Ti and Mo and between Mo and W would be desirable. In each case 100-mg amounts of these elements were taken. It was reasoned that separations more suitable for practical application could be achieved with smaller amounts without increasing the column lengths. It was decided, therefore, to verify the separations listed in Table III experimentally by applying them to mixtures containing 70 mg each of the appropriate elements and approximately 900 mg of Cb.

The mixtures were dissolved in 30 ml of 3 M HF, transferred to appropriate preconditioned columns, and eluted in accordance with the scheme being tested. Fractions were collected and tested qualitatively in order to follow the elution of each element. The relative amount of each element in its respective fractions was estimated on the basis of visual comparison. This information was used to prepare elution curves to illustrate the various separations graphically. Since all the curves are based on qualitative data, the elution of Cb with 3 M  $\text{NH}_4\text{Cl}$ -1 M HF was included in each case.

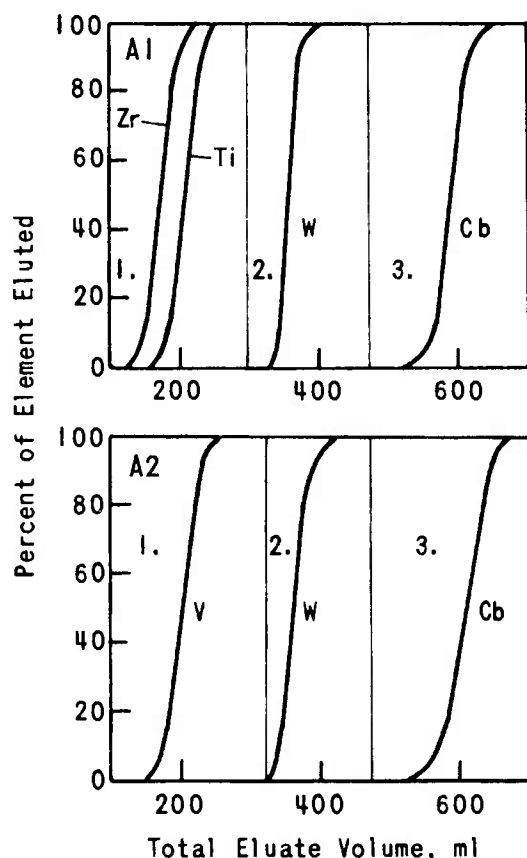


Figure 13. SEPARATION SCHEME A, USING 11-CM X 5-SQ CM COLUMN

A1 Separation of Zr and Ti, W (70 mg each), and Cb (900 mg)  
A2 Separation of V, W (70 mg each), and Cb (900 mg)

ELUTING SOLUTIONS: 1. 27.5 M HF; 2. 7 M HCl-3 M HF;  
3. 3 M  $\text{NH}_4\text{Cl}$ -1 M HF.

The separation of Zr and Ti, W, and Cb and of V, W, and Cb employing Scheme A is illustrated in Figure 13. Note that the elution curves are separated by convenient intervals for practical application. Figure 14 shows the separation of V, Zr and Ti, and Cb by means of Scheme B. The elution of Zr and Ti could have been accomplished with 3 M HCl-5.8 M HF as well as 7 M HCl-3 M HF.<sup>8</sup>

Separations employing Scheme C are shown in Figures 15 and 16. Satisfactory separations with approximately 50-ml intervals between elution curves were achieved in each case, except for the separation of Ti and Mo from a mixture of Zr, Ti, Mo, W, and Cb, shown in Figure 15, Separation C3. In this case Ti and Mo are separated by approximately 25 ml.

According to Table III, Scheme C employs a 21-cm column and 27.5 M HF followed by 7 M HCl-3 M HF as eluents. The latter eluent is used to elute W when W is present in the original mixture. Obviously this step can be eliminated when W is absent (see Separation C2, Figure 15, and C5, Figure 16). In each of the separations shown in Figures 15 and 16, Mo is eluted with 27.5 M HF. When W is absent, Mo can be eluted with 3 M HCl-5.8 M HF if desired, to keep the use of 27.5 M HF down to a minimum. The 7 M HCl-3 M HF is not a suitable eluent for Mo.<sup>9</sup>



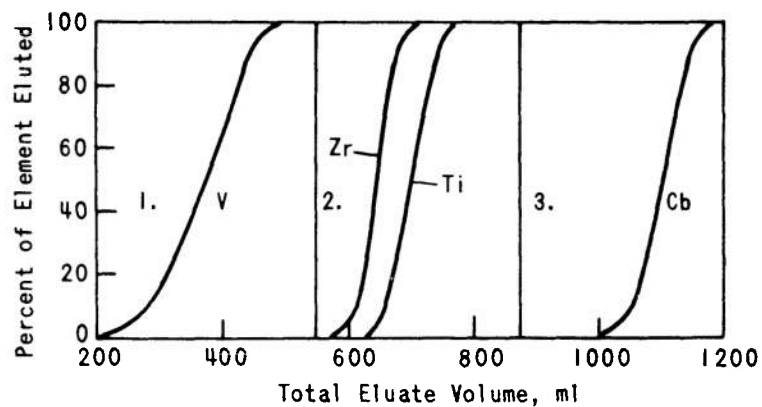


Figure 14. SEPARATION SCHEME B, USING 12.5-CM X 5-SQ CM COLUMN  
Separation of V, Zr and Ti (70 mg each), and Cb (900 mg)

ELUTING SOLUTIONS: 1. 10.1 M HF; 2. 7 M HCl-3 M HF; 3. 3 M  $\text{NH}_4\text{Cl}$ -1 M HF.

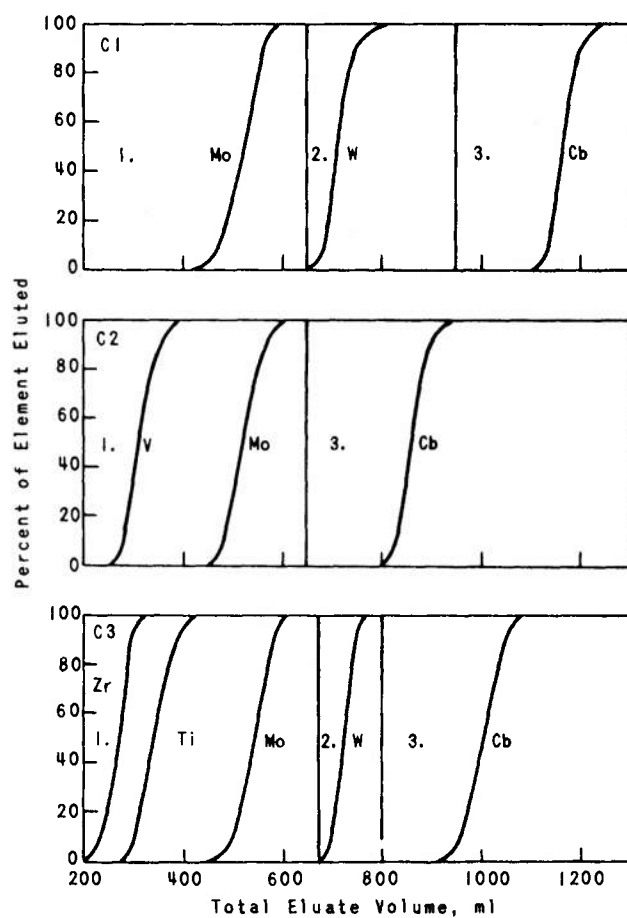


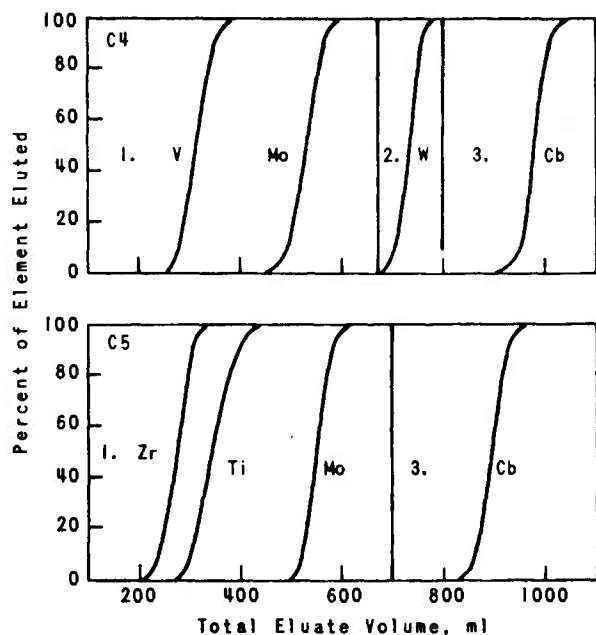
Figure 15. SEPARATION SCHEME C, USING  
21-CM X 5-SQ CM COLUMN

C1 Separation of Mo, W (70 mg each), and Cb (900 mg)

C2 Separation of V, Mo (70 mg each), and Cb (900 mg)

C3 Separation of Zr and Ti, Mo, W (70 mg each), and Cb (900 mg)

ELUTING SOLUTIONS: 1. 27.5 M HF; 2. 7 M HCl-3 M HF; 3. 3 M  $\text{NH}_4\text{Cl}$ -1 M HF.



**Figure 16. SEPARATION SCHEME C, USING 21-CM X 5-SQ CM COLUMN**

C4 Separation of V, Mo, W (70 mg each), and Cb (900 mg)

C5 Separation of Zr and Ti, Mo (70 mg each), and Cb (900 mg)

ELUTING SOLUTIONS: 1. 27.5 M HF; 2. 7 M HCl-3 M HF; 3. 3 M  $\text{NH}_4\text{Cl}$ -1 M HF.

The resolution of mixtures of V, Mo, and Cb and of Zr and Ti, Mo, and Cb is shown in Figure 15, Separation C2, and Figure 16, Separation C5. It was calculated earlier that the separation of small amounts of Ti and Mo with 27.5 M HF could be accomplished with a 13.2-cm column. However, in view of the proximity of the elution curves of Ti and Mo in Figures 10 and 12, a column shorter than 21 cm could not be expected to provide enough latitude in the separation of these two elements. The same would apply to the separation of V and Mo since the elution behavior of V and Ti in 27.5 M HF is practically identical (see Figure 9). An interval of 50 ml was actually realized in each case by employing a 21-cm column.

The separations shown in Figure 17 were accomplished by means of coupled columns (Scheme D). Note the improved latitude of 25 ml between the elution curves of Ti and Mo as compared with Figure 12. Apparently, unless a greater interval is desired, the length of the second section need not be increased for handling 70 mg or smaller amounts.

For the separation of V, Zr and Ti, Mo, and Cb, shown in Figure 17, Separation D3, elution through the coupled columns with 27.5 M HF was continued until Mo began to elute. At this point, the sections were disconnected and the remainder of the Mo in the lower 18-cm section was eluted with 27.5 M HF, while Cb was removed from the 12.5-cm section as usual.

The one combination for which a separation scheme is not illustrated is that of V, Zr and/or Ti, W, and Cb. This mixture can be readily resolved by means of a single 12.5-cm column. The V and Zr and/or Ti would be removed with 10.1 M HF and 27.5 M HF, respectively, as in Scheme B and shown in Figure 14. The W and Cb would then be eluted as usual.

## DISCUSSION

From a practical standpoint it must be remembered that variations in flow rate, column length, and particle size will affect the ion-exchange behavior of the elements. Differences may even be observed with different lots of the same resin. In applying the schemes developed herein to analytical problems, given the same type resin, it should be possible to duplicate the separations, provided the same experimental conditions are maintained.

However, for routine applications, wider intervals between successive solutes may be desired to allow for differences in the relative amounts of solutes to be separated and for such

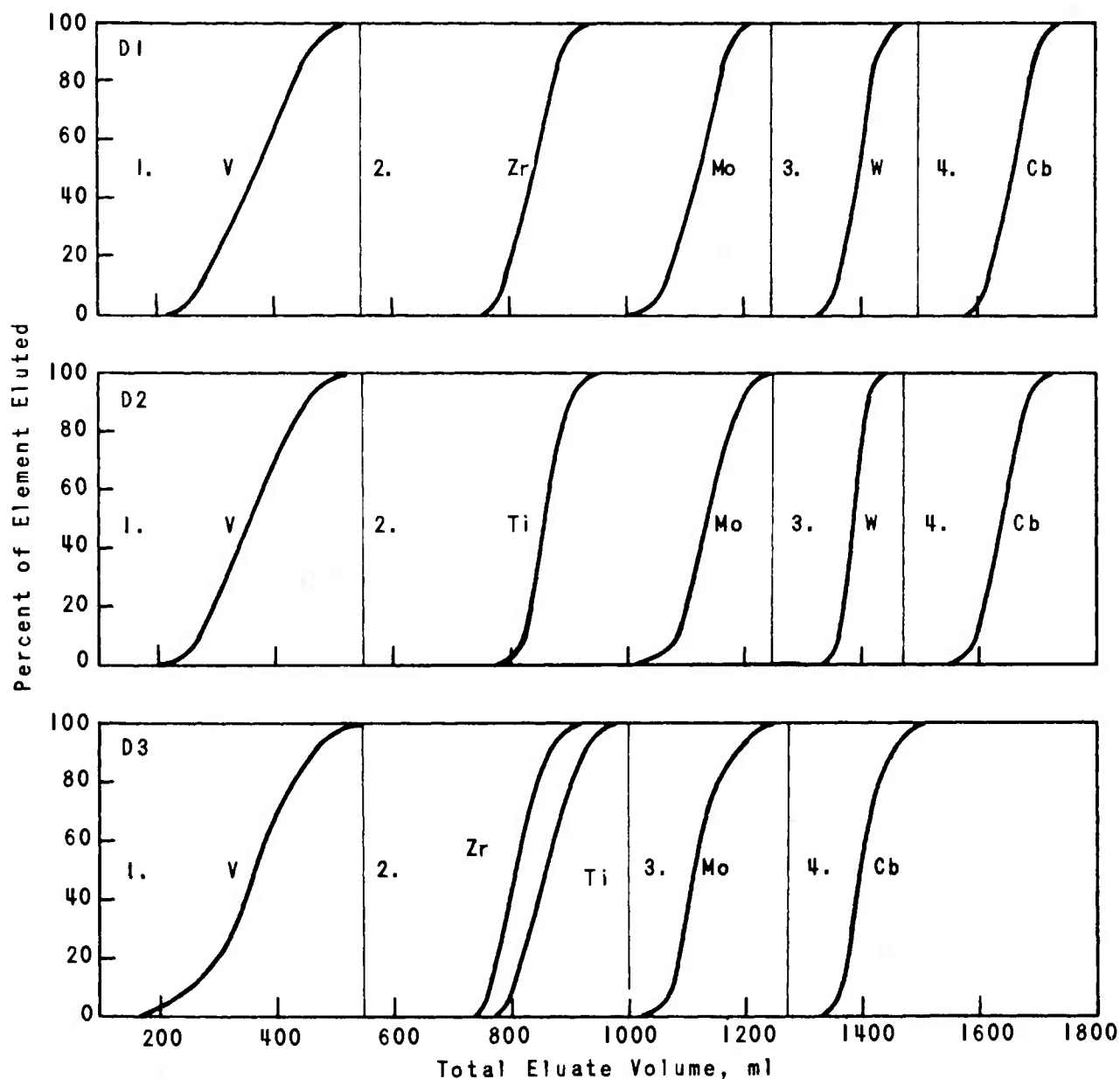


Figure 17. SEPARATION SCHEME D

D1 Separation of V, Zr, Mo, W (70 mg each), and Cb (900 mg)

D2 Separation of V, Ti, Mo, W (70 mg each), and Cb (900 mg)

D3 Separation of V, Zr, Ti, Mo (70 mg each), and Cb (900 mg)

ELUTION SEQUENCE:

1. Elution of V through a 12.5-cm column with 10.1 M HF.
2. D1 and D2, elution of Zr, Ti and Mo through coupled 12.5-cm and 18-cm columns with 27.5 M HF.  
D3, elution of Zr, Ti and portion of Mo through coupled column with 27.5 M HF.
3. D1 and D2, elution of W through lower 18-cm column with 7 M HCl-3 M HF.  
D3, elution of Mo through lower 18-cm column with 27.5 M HF.
4. Elution of Cb through 12.5-cm column with 3 M  $\text{NH}_4\text{Cl}$ -1 M HF.

incidental differences as may occur in flow rate and sample and washing volumes. With this in mind, simplified equations were derived which allow the calculation of the column length needed to provide any desired theoretical interval in the separation of V and Zr, Ti and Mo, and Mo and W with the appropriate eluents, since these are the critical separations.

The separation of two solutes is dependent upon the trailing edge of the solute which elutes first and the leading edge of the next solute. The elution of the first solute is complete at  $U_1^* + U_1$ , where  $U_1$  can be determined for the trailing edge of the first solute by means of Equation 10. The elution of the next solute begins at  $U_2^* - U_2$ , where  $U_2$  is determined for the leading edge of the second solute. The interval between the solutes, then, is equal to  $(U_2^* - U_2) - (U_1^* + U_1)$ .

It has been shown that the interstitial volume,  $V$ , is equal to 46 percent of the column volume, and is therefore equal to  $2.3 H$  for a column 2.5 cm in diameter. Substituting this in Equation 1 it can be shown that  $U_2^* - U_1^* = 2.3 H (C_2 - C_1)$ . The interval then becomes  $2.3 H (C_2 - C_1) - U_2 - U_1$ . By means of the data listed in Tables I and II and by employing Equation 10 to calculate  $U_2$  and  $U_1$ , interval equations for the separations mentioned above were obtained in which the interval is expressed as a function of column length. These are shown in Table IV.

Table IV. EQUATIONS DEFINING SEPARATION INTERVALS  
IN TERMS OF COLUMN HEIGHT

Elements Separated	V and Zr	V and Zr	Ti and Mo	Mo and W
Eluent	8.7 M HF	11.6 M HF	27.5 M HF	27.5 M HF
Interval Equation	$66 H - 145 \sqrt{H}$	$22.6 H - 78 \sqrt{H}$	$8.8 H - 30 \sqrt{H}$	$11 H - 48 \sqrt{H}$

According to the interval equation for the separation of Ti and Mo with 27.5 M HF, the column length calculated by Equation 4 for this separation, 13.2 cm, would provide a theoretical interval of 7 ml. This is hardly adequate for practical application. If an interval of 100 ml is desired, the required column length can be determined by setting the interval equation equal to 100 and solving for  $H$ :  $8.8 H - 30 \sqrt{H} = 100$ . The column height so determined is 30 cm. A 21-cm column would provide an interval of 48 ml. The interval actually obtained with 70-mg amounts was 50 ml, as shown in Figure 15, Separation C2, and Figure 16, Separation C5.

It would be preferable, then, to determine the required column length on the basis of the desired interval rather than on the basis of Equation 4. By modification of Equation 4 to provide a higher degree of purity, the calculated column length is, of course, larger. It was pointed out earlier that substitution of the value 3.74 in place of 3.29 provides for a purity of 99.99 percent. For the separation of Ti and Mo the calculated column length becomes 17 cm. According to the interval equation this length would provide a separation of 27 ml. Thus, where a separation of 50 ml is desired, Equation 4 does not provide an adequate column length even with this higher criterion of purity.

The interval equation is also useful for determining how much the column length should be increased when overlapping occurs due to overloading. The column length determined earlier by Equation 4 for the separation of V and Zr with 8.7 M HF was 5.3 cm. This was increased to 6 cm to allow for loading conditions. According to the interval equation for this separation a 6-cm column should separate these elements by 40 ml. The experimental elution curves shown in

Figure 5 actually overlap to the extent of approximately 135 ml. The difference between the actual and theoretical intervals obtained with the 6-cm column amounts to about 175 ml. For a desired separation of 50 ml, it should be possible to determine the required column length by setting the interval equation equal to  $175 + 50$  or 225 ml. The column height so determined is 10.5 cm.

This estimate, which is based upon a single elution experiment with a 6-cm column, is quite impressive when one considers the actual experimental results obtained with a 9-cm column, where an overlap of only 50 ml was observed. This approach should prove useful to column separations in general where column loading is high and overlapping occurs.

In the separation of 100-mg amounts of Ti, Mo, and W, in the presence of 700 mg of Cb with a 21-cm column and 27.5 M HF, there was very little latitude between Ti and Mo and between Mo and W (Figure 10). According to the interval equations an improvement of 32 ml in the separation of Ti and Mo and of 38 ml between Mo and W would be achieved with a 27-cm column.

### CONCLUSIONS

1. The ion-exchange separation schemes developed herein for the group of elements V, Zr and Ti, Mo, W, and Cb, unlike other existing methods, are applicable in the presence of relatively large amounts of Cb. Moreover, the proposed methods provide for the separation of V, and sample preparation is convenient since a hydrofluoric acid medium is employed.

2. The divergence of the adsorption behavior of Mo and W toward high hydrofluoric acid concentrations, as indicated by the data published by Faris,<sup>8</sup> was shown to persist above the maximum concentration of this acid studied by Faris. This made possible the extension of the hydrofluoric acid system to include the separation of Mo from W without having to resort to the hydrochloric-hydrofluoric acid system with which large amounts of Cb interfere.

3. It has been shown that coupled columns can be employed to improve the efficiency of ion-exchange column separations of multicomponent mixtures.

4. The proposed separation methods should be particularly suitable for application to the chemical analysis of Cb-base alloys and Cb-bearing Ta-base alloys.

5. The theoretical interval between the elution curves of two solutes can be expressed in equation form as a function of column height. By means of this equation, the interval or latitude desired in the separation of these solutes can serve as a useful criterion in determining the required column length. The interval equation also provides a convenient means for calculating how much the column length should be increased when overlapping occurs due to overloading of the column.

APPENDIX I  
SEMI-QUANTITATIVE CHEMICAL TESTS EMPLOYED

Element	Treatment	Positive Test	Least Amount Detectable mg/25 ml
V*	To 10 ml of fraction added $\frac{1}{2}$ ml $\text{H}_2\text{SO}_4$ plus a few drops of $\text{HNO}_3$ . Evaporated to fumes. Added 3 drops of 30% $\text{H}_2\text{O}_2$ .	Brown color	Approximately 0.1
Zr*	To 10 ml of fraction added 2 ml $\text{HClO}_4$ plus a few drops of $\text{HNO}_3$ . Evaporated and fumed until volume down to few drops. Added 8 ml $\text{H}_2\text{O}$ and 3 ml $\text{HCl}$ , heated, then added 5 ml of 0.1% solution of alizarin red S.	Red color	Approximately 0.1
Ti	To 5 ml added 1 ml $\text{H}_2\text{SO}_4$ plus a few drops of $\text{HNO}_3$ , and heated to fumes. Added 9 ml $\text{H}_2\text{O}$ and 3 drops of 30% $\text{H}_2\text{O}_2$ .	Yellow color	Less than 0.1
Mo	To 5 ml added 4 ml of 25% solution of $\text{SnCl}_2$ and 2 ml of 10% solution of $\text{NaSCN}$ .	Red-brown color	Approximately 0.1
W*	To 20 ml added $\frac{1}{2}$ ml $\text{H}_2\text{SO}_4$ . Heated to fumes. Added 2 ml $\text{H}_2\text{O}$ and 3 ml of 25% solution of $\text{SnCl}_2$ .	Blue precipitate	Approximately 0.3
Cb*	To 5 ml added $\frac{1}{2}$ ml $\text{H}_2\text{SO}_4$ . Heated to fumes. Added 3 ml $\text{H}_2\text{O}$ and 3 ml $\text{NH}_4\text{OH}$ .	White precipitate	Approximately 0.3

\*These chemical tests were applied as written only to fractions containing small amounts of the elements involved in order to locate exactly where the first and last portions of each element appeared in the eluate. Otherwise smaller portions were taken and fuming omitted in the case of vanadium and columbium in order to first locate the fractions containing the major portion of each element.

NOTE: For fractions where V and Ti might be present together,  $\text{HF}$  was added after testing for Ti with  $\text{H}_2\text{O}_2$ . The yellow color due to titanium is bleached out, while the brown color due to vanadium remains.

APPENDIX II  
REAGENTS USED IN PHOTOMETRIC QUANTITATIVE TESTS

Element	Reagent	Medium
V	$\text{H}_2\text{O}_2$	20% $\text{H}_2\text{SO}_4$
Zr	Xylenol Orange	0.5% $\text{H}_2\text{SO}_4$
Ti	$\text{H}_2\text{O}_2$	10% $\text{H}_2\text{SO}_4$
Mo	$\text{H}_2\text{O}_2$	10% $\text{HClO}_4$ -10% $\text{H}_3\text{PO}_4$
W	$\text{NaSCN}$	50% $\text{HCl}$

## LITERATURE CITED

1. HAGUE, J. L., BROWN, E. D., and BRIGHT, H. A. *Separation of Titanium, Tungsten, Molybdenum, and Niobium by Anion Exchange*. Journal of Research, National Bureau of Standards, v. 53, 1954, p. 261-262.
2. HAGUE, J. L., and MACHLAN, L. A. *Determination of Niobium and Tantalum in Titanium-Base Alloys*. Journal of Research, National Bureau of Standards, v. 62, 1959, p. 53-57.
3. WILKINS, D. H. *The Separation and Determination of Nickel, Chromium, Cobalt, Iron, Titanium, Tungsten, Molybdenum, Niobium and Tantalum in a High-Temperature Alloy by Anion Exchange*. Talanta, v. 2, 1959, p. 355-360.
4. DIXON, E. J., and HEADRIDGE, J. B. *The Anion-Exchange Separation of Titanium, Zirconium, Niobium, Tantalum, Molybdenum and Tungsten, with Particular Reference to the Analysis of Alloys*. Analyst, v. 89, 1964, p. 185-204.
5. BANDI, W. R., BUYOK, E. G., LEWIS, L. L., and MELNICK, L. M. *Anion Exchange Separation of Zirconium, Titanium, Niobium, Tantalum, Tungsten and Molybdenum*. Analytical Chemistry, v. 33, 1961, p. 1275-1278.
6. KALLMANN, S. *Spectrophotometric Determination of Trace Amounts of Zirconium, Titanium, and Molybdenum in Tungsten*. Analytical Chemistry, v. 36, 1964, p. 2358.
7. HELFFERICH, F. *Ion Exchange*. McGraw-Hill Book Company, Inc., 1962, p. 487.
8. FARIS, J. P. *Adsorption of the Elements from Hydrofluoric Acid by Anion Exchange*. Analytical Chemistry, v. 32, 1960, p. 520-522.
9. FARIS, J. P., and BRODY, J. K. *Adsorption of the Elements from HCl-HF Mixtures*. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Paper 34, February 1961.
10. CORNISH, F. W. *The Practical Application of Chromatographic Theory to Analytical and Preparative Separations by Ion-Exchange Elution*. Analyst, v. 83, 1958, p. 634-642.
11. BERL, W. G., ed., *Physical Methods in Chemical Analysis*, Vol. IV. Academic Press, New York & London, 1961, p. 133-222.
12. See Reference 7, p. 457.
13. SAMUELSON, O. *Ion Exchange Separations in Analytical Chemistry*. John Wiley and Sons Inc., New York & London, 1963, p. 125.
14. GLUECKAUF, E. *Theory of Chromatography: Part 9 - The Theoretical Plate Concept in Column Separations*. Transactions of the Faraday Society, v. 51, 1955, p. 34-44.
15. See Reference 13, p. 209.
16. HIBBS, L. E., and WILKINS, D. H. Talanta, v. 2, 1959, p. 16.
17. See Reference 13, p. 226.

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<p>The elution behavior of vanadium, zirconium, titanium, molybdenum, tungsten, and columbium was studied at various hydrofluoric acid concentrations employing a strong base anion exchange resin. The results of this study were used to establish appropriate separation schemes. Coupled columns were employed for the separation of the complete group. Simple columns were used for less complicated mixtures. Vanadium, zirconium, titanium, and molybdenum were eluted with appropriate hydrofluoric acid solutions. In this way, interference from large amounts of columbium was avoided.</p> <p>An "interval" equation defining the desired volume interval between successively eluting solutes is offered for calculating the column length required for a particular separation. This equation is especially useful for determining the extent to which a column must be lengthened when overlapping occurs due to high column loading. (Author)</p>		

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